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OPTICAL CHARACTERIZATION OF ATMOSPHERIC PARTICULATES ON SAN NIC--ETC(U)
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OPTICAL CHARACTERIZATION OF ATMOSPHERIC PARTICULATES ON SAN NICOLAS ISLAND, CALIFORNIA

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By

B. D. HINDS

J. B. GILLESPIE

US Army Electronics Research and Development Command
ATMOSPHERIC SCIENCES LABORATORY
White Sands Missile Range, NM 88002

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ASL-TR-0053	2. GOVT ACCESSION NO. AD A103 376	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) OPTICAL CHARACTERIZATION OF ATMOSPHERIC PARTICULATES ON SAN NICOLAS ISLAND, CALIFORNIA		5. TYPE OF REPORT & PERIOD COVERED R&D Technical Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) B. D. Hinds J. B. Gillespie		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Atmospheric Sciences Laboratory White Sands Missile Range, New Mexico 88002		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS DA Task 1L161102B53A/13
11. CONTROLLING OFFICE NAME AND ADDRESS US Army Electronics Research and Development Command Adelphi, MD 20783		12. REPORT DATE April 1980 13. NUMBER OF PAGES 21
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Imaginary index
Aerosols
Aerosol sampling

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The US Army Atmospheric Sciences Laboratory at White Sands Missile Range, New Mexico, analyzed eight atmospheric particulate samples and one soil and one abalone shell sample taken on San Nicolas Island. These samples were collected by the Naval Weapons Center and Pacific Missile Test Center meteorological personnel for composition and average imaginary refractive index analyses in the visible and infrared spectral region. This report covers the time period of 22 October 1978 through 10 May 1979.

ACKNOWLEDGMENTS

Our sincere appreciation is extended to Mr. Manuel Bustillos for his untiring laboratory assistance, to Mr. Armando Perez for his drafting support, and to Mr. Robert Bonner and Dr. Donald E. Snider for their cooperation and report review. We also thank Mr. Bob Horigan of the National Aeronautics and Space Administration for his cooperative support in the composition elemental analysis.

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INTRODUCTION

The Electro-Optical (EO) Division of the Atmospheric Sciences Laboratory (ASL), White Sands Missile Range (WSMR), New Mexico, was requested by the Naval Weapons Center (NWC), China Lake, and the Navy Electro-Optical Meteorology Program, with Headquarters at the Naval Ocean Systems Center, to participate in their marine optical signature program. Navy personnel collected several samples of atmospheric particulate matter on 0.45μm pore size cellulose membrane filters.[1] These filters were returned to ASL for determination of average imaginary refractive index[2] in the 0.3μm to 1.7μm spectral region and for composition. The composition analysis was used to infer the complex refractive index in the 9μm to 11μm spectral region. These data are to be used to characterize the aerosol during the tests at San Nicolas Island (SNI) so that calculational comparisons with the transmission measurements can be made. Some meteorological quantities are also included to emphasize the environmental effects. The sample collection period covered in this report is 22 October 1978 through 10 May 1979.

SNI, approximately 120 km southwest of Los Angeles, California, was the project site (figure 1*). The SNI station number on the meteorological summary is 93116 (WMO number is 72291).[3] SNI latitude (ϕ), longitude (λ), and elevation (ϵ), in meters, above mean sea level (MSL), are:

$$\phi = 33^\circ\ 14.5'\ \mathrm{N}$$

$$\lambda = 119^\circ\ 28.0'\ \mathrm{W}$$

$$\epsilon = 153.6\ \mathrm{m}$$

Table 1 presents a climatic summary of SNI, and table 2 presents the percent frequency visibility at SNI.[4] One of the most outstanding features of table 1 is the wind direction and peak gust speed. The wind direction is always from the north, northwest, or west-northwest, with

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[1]C. Petracca and J. Lindberg, 1975, Installation and Operation of an Atmospheric Particulate Collector, ECOM 5575, Atmospheric Sciences Laboratory, White Sands Missile Range, New Mexico

[2]J. D. Lindberg and L. S. Laude, 1974, Measurement of the Absorption Coefficient of Atmospheric Dust, Applied Optics, 13:1923-1927

*Figures and tables are presented at end of text

[3]Summary of Meteorological Observations, Surface (SMOS) San Nicolas Island, California Naval Weather Service Detachment Federal Building, Asheville, NC, AD A060-999

[4]Robert deViolini, 1975, Climatic Summary for the Pacific Missile Test Center, TP-75-25, Pacific Missile Test Center, Point Mugu, California

the peak gust speed ranging between 38 to 52 knots. The aerosol collector was located on a tower approximately 3 meters above the surface at site A (figure 2):

$$\phi = 33° \ 16' \ 37'' \ \mathrm{N}$$

$$\lambda = 119° \ 34' \ 31'' \ \mathrm{W}$$

$$\varepsilon = 9.5 \ \mathrm{m}$$

Table 2 indicates that during the sampling period the visibility was approximately 16 km over 55 percent of the time. If this visibility were translated into particulate aerosol mass concentration (c), it would indicate a maximum value of 100 micrograms per cubic meter.[5] This value is equivalent to the mass concentration of a continental air mass;[6] however, some of the aerosol in a maritime environment would be liquid droplets, and the measured values given in this report are only for the solid particulates due to the aerosol sampling method used.

ANALYSIS AND RESULTS

Table 3 summarizes the available data and analysis associated with each collected sample. One feature of this table shows the computed average mass concentration for each sample in micrograms per cubic meter. This quantity is given to indicate the lower limit of sampled particulate concentration in a maritime air mass environment. The mass concentration as previously computed by using visibility values would represent a higher limit.

Variability between the measured and calculated mass concentration is related primarily to water droplet content and secondarily to loss of some of the water soluble fraction because of the sampling procedure used. For additional sampling site data base information, SNI prevailing meteorological conditions are summarized in the appendix.[7]

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[5]R. J. Charlson, N. C. Ahlquist, H. Selvide, and P. B. MacCready, Jr., 1969, J Air Poll Control Assoc, 19:937

[6]W. J. Lentz and G. B. Hoidale, 1974, Estimates of the Extinction of Electromagnetic Energy in the 8 to 12 μm Range by Natural Atmospheric Particulate Matter, ECOM 5528, Atmospheric Sciences Laboratory, White Sands Missile Range, New Mexico

[7]G. B. Matthews and B. E. Williams, compilers, 1978, Atmospheric Transmission and supporting Meteorology in the Marine Environment at San Nicolas Island, Semiannual Report TP-79-19, Pacific Missile Test Range, Point Mugu, California

Table 3 also itemizes how the samples were processed. An acetone washing technique was used on samples 1, 2, and 3 to remove the collected particulates from the 47 mm cellulose acetate filter for making the imaginary refractive index measurement. In this processing technique, the filter is placed in a centrifuging test tube and dissolved with acetone; then the particulates are precipitated out by the use of a high-speed centrifuge. This process is repeated three times. Most of the liquid is removed after each centrifuging with a 15-milliliter syringe and placed in an evaporating dish. The residue remaining in the dish indicates two things: if there is any filter left in the test tube and if any particulate material has been washed out. In samples 6 through 10, the acetone process was not used. Instead, a filter segment was brushed with potassium bromide (KBr) which is used as a matrix lattice for holding the sample when pressed into a 13 mm diameter pellet approximately 0.8 mm thick for a transmission measurement. This latter sample preparation gives greater confidence in detecting organic material in the sample, even though this method will probably bias the sample toward the larger particle fraction of the collected aerosols.

Atmospheric samples were chemically analyzed by three instrumental techniques. The sample was elementally analyzed by using a scanning electron microscope (SEM), crystalline structure analyzed by using an X-ray diffraction (XRD) technique, and molecularly analyzed by an infrared spectrometer. From these analyses, magnesium calcium carbonate ($Mg_3Ca[CO_3]_4$) and hydrated calcium carbonate ($Ca[CO_3]_2[OH]_2 1.5H_2O$) were predominant. One likely source of this material is the abalone shells which are in abundance on the upwind shoreline near the sampler.* SEM soil and abalone sea shells were analyzed for mineral content. The soil contained 73 percent calcite, 17 percent sand, 7 percent potassium, 3 percent aluminum, while the abalone sea shells were essentially 100 percent $CaCO_3$. Note that $CaCO_3$ is combined with $MgCl_2$ to form dolomite ($CaMg[CO_3]_2$) by the reaction $2CaCO_3 + MgCl_2 = CaMg(CO_3)_2 + CaCl_2$, and this reaction takes place either before or after it emerges from the sea.[8] The XRD analysis is shown in table 4. Other minerals such as sodium chloride (NaCl) and ammonium sulfate ($[NH_4]_2SO_4$) may have been present; however, because of insufficient sample quantity, the presence of these minerals could not be verified. It is believed that the amount of NaCl would be small because of the solubility of the mineral and because the filters became wet several times during the sampling period. The third instrumental technique analyzed the sample for molecular composition by an infrared grating spectrophotometer. This instrument shows the transmission "fingerprint" of a sample between

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*Robert S. Bonner, unpublished data, personal communication, 1979, Atmospheric Sciences Laboratory, White Sands Missile Range, NM

[8]E. H. Kraus, W. F. Hunt, and L. S. Ramsdell, 1959, Mineralogy, McGraw-Hill Book Company, Inc., New York, p 330

spectral region 2.5μm to 40μm wavelengths (figure 3). From the spectral "fingerprint," the San Nicolas Island sample differed primarily in the mineral concentration. It showed the presence of some nitrate (NO_3) ions near 7.2μm wavelengths and hinted at a very weak sulfate (SO_4) ion at about 16.6μm wavelengths. Its spectral "fingerprint" indicated the possible presence of several other minerals with similar elemental characteristics. These atmospheric collected aerosol minerals and soil sample minerals are listed in table 4. Around the island is an abundant cyclic growth of kelp. Even though its growing season and growth rates are not presently available, sodium iodate ($NaIO_3$) was checked for its spectral transmission dependence fingerprint. There were no correlations.

Table 5 shows the average imaginary refracive index of three samples measured from a diffuse reflectance spectrophotometer. The tabularized data compare samples 1, 2, and 3 between wavelengths of 0.3μm to 1.7μm in incremental steps of 0.2um. These values of the average imaginary refractive index in the visible and the lack of any strongly absorbing mineral in the infrared transmission spectral region indicates that materials such as free carbon are equal to or less than approximately 0.2 percent of the total mass of the sample.

SUMMARY AND COMMENTS

At the present time there is no satisfactory method of measuring complex refractive indices of powdered samples of mixed components. The diffuse reflectance spectroscopy method offers the best method of determining the average of the imaginary part of the complex refractive index of the mixture; however, this method is currently only applicable in the visible and near infrared. From the composition analysis, reasonable average values of complex indices (m) to be used for the samples are inferred. For the components determined ($CaSO_4 2H_2O$), a value of $m = 1.5 - 0.001i$ is a reasonable value to use in the visible and near infrared; while for values in the 9μm to 11μm spectral region, Querry et al[9] have found calcium carbonate limestone values of about $m = 1.68 - 0.187i$. This value, however, is limited in use since airborne maritime calcium carbonate has a different source than the limestone soil material, but it is probably a reasonable estimate to try in atmospheric propagation calculations. Jennings and Gillespie[10] discuss

[9]M. R. Querry, G. Osborne, K. Lies, R. Jordan, and R. M. Coveney, Jr., 1978, Complex Refractive Index of Linestone in the Visible and Infrared, Applied Optics, 17:353-356

[10]S. G. Jennings and J. B. Gillespie, 1978, Mie Theory Sensitivity Studies - The Effects of Aerosol Complex Refractive Index and Size Distribution Variation on Extinction Absorption Coefficients, Part II: Analysis of the Computation Results, ASL-TR-0003, Atmospheric Sciences Laboratory, White Sands Missile Range, New Mexico

the effect of uncertainty in the knowledge of real and imaginary parts of the complex refractive index upon Mie calculations, and Jennings and Pinnick[11] discuss the more commonly occurring atmospheric aerosols.

Aerosol samples collected on the met tower site A (elevation 9.5 m above sea level) show evidence of minerals which are also found in the surrounding soil. Although this occurrence may be due to the effects of local contamination, it is not possible to determine uniquely the origin of this material. Measurements of radon 222 (^{222}Rn) indicate that SNI is from time to time under the influence of a continental air mass. Results presented here do not contradict that conclusion.

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[11]S. G. Jennings, R. G. Pinnick, and H. J. Auvermann, 1978, Effects of Particulate Size Distribution Variations on Atmospheric Extinction and Absorption for Visible Through Middle IR Wavelengths, Applied Optics, 17(4): Number 24

TABLE 1. SAN NICOLAS ISLAND SURFACE CLIMATIC SUMMARY[a]

Month	Temperature Average Max	Temperature Average Min	Precipitation Average Amount (in.)	Humidity Average (%) Max	Humidity Average (%) Min	Surface Winds (knots) Prevailing Direction	Surface Winds (knots) Average Speed	Surface Winds (knots) Peak Gust Direction	Surface Winds (knots) Peak Gust Speed	Mean Sky Cover (1/10)
January	59.3	48.1	1.47	86	59	NW	12	WNW	52	4.6
February	60.5	48.8	1.21	88	60	NW	14	NW	40	4.5
March	59.8	48.2	0.76	88	59	NW	15	WNW	43	4.6
April	62.4	49.6	0.64	87	58	NW	15	NW	42	4.3
May	63.2	51.0	0.06	90	64	NW	16	WNW	42	5.2
June	65.1	53.1	0.02	93	66	NW	14	WNW	45	5.4
July	68.7	55.6	0.01	94	65	NW	13	NW	45	5.1
August	70.2	56.8	Trace	94	63	NW	13	WNW	41	4.6
September	71.1	57.7	0.04	89	59	NW	13	WNW	39	4.5
October	68.8	52.7	0.14	86	57	NW	12	NW	41	4.0
November	65.2	52.6	1.18	86	58	NW	12	N	38	4.2
December	60.6	49.4	1.01	85	58	NW	12	NW	42	4.0
Year Average or Peak Value	64.6	52.0	6.55	88	61	NW	14	WNW	52	4.6

[a]Robert deViolini, 1975, Climatic Summary for the Pacific Missile Test Center, TP-75-25, Pacific Missile Test Center, Point Mugu, California

TABLE 2. PERCENT FREQUENCY OF SELECTED VISIBILITY AT SAN NICOLAS ISLAND[4]

MONTH	VISIBILITY FREQUENCY (PERCENT)						
	KM	< 0.8	< 1.6	≤ 9.7	≤ 16.1	≤ 16.6	X
JANUARY		4.9	6.1	90.6	83.6	65.0	
FEBRUARY		3.8	5.2	91.2	83.1	66.0	66.0
MARCH		1.5	2.3	95.2	84.8	68.5	68.5
APRIL		1.8	2.5	95.3	79.8	56.2	56.2
MAY		2.6	3.7	90.5	72.0	45.9	45.9
JUNE		3.6	5.6	87.3	63.2	38.3	
JULY		3.8	7.5	85.4	67.0	24.1	
AUGUST		4.0	6.2	86.2	54.7	23.8	
SEPTEMBER		2.4	3.6	89.7	62.4	30.7	
OCTOBER		2.9	4.2	90.8	68.8	41.1	41.1
NOVEMBER		2.3	3.3	92.6	79.1	57.2	57.2
DECEMBER		4.4	5.7	90.9	80.4	61.5	
YEAR		3.2	4.6	90.4	71.9	47.6	55.8

[4]Robert deViolini, 1975, Climatic Summary for the Pacific Missile Test Center, TP-75-25, Pacific Missile Test Center, Point Mugu, California

X indicates the months when atmospheric particulate aerosols were collected.

TABLE 3. SAN NICOLAS ISLAND COLLECTED AIR SAMPLES AND ANALYSIS

Sample No.	Collection Period [Day Month:Year(time)]	Mass Concentration ($\mu gm/m^3$)	Acetone Wash	SEM and XRD	IR	m
1	28 10:78(0900) → 2 11:78(1300)	23.9	√		√	√
2	2 11:78(1305) → 14 11:78(0900)	15.0	√		√	√
3	14 22:78(0900) → 22 11:78(--)	30.9	√	√	√	√
6	1 2:79(1050) → 21 2:79(1100)	11.9			*	
7	21 2:79(1100) → 14 3:79(1010)	12.9			*	
8	14 3:79(1010) → 12 4:79(1055)	7.4			*	
9	12 4:79(1055) → 1 5:79(1100)	6.7			*	
10	1 5:79(1100) → 10 5:79(1000)	22.3			*	
11	Soil sample near site A			√	√	
12	Abalone shell sample			√	√	

Legend:

SEM = scanning electron microscope
XRD = X-ray diffraction
IR = infrared
m = average imaginary refractive index
* = segment of filter brushed to collect particulate for IR analysis

TABLE 4. SIMILAR MINERAL SPECTROPHOTOMETRIC TRANSMISSION CHARACTERISTICS AS FOUND ON SAN NICOLAS ISLAND AND XRD SOIL ANALYSIS

Minerals	Refractive Index At Visible Wavelengths	Average Specific Gravity
Aerosol Sample		
Dolomite	1.681	2.85
Magnesite	1.70	3.06
Hydromagnesite	1.527	2.16
Sand	1.544	2.65
Calcite	1.658	2.72
Soil Sample		
Wollastonite	1.627	2.86
Andalusite	1.638	3.15
Feldspar	1.544	2.64

TABLE 5. AVERAGE IMAGINARY REFRACTIVE INDEX OF SAN NICOLAS ISLAND ATMOSPHERIC SAMPLES

Wavelength (μm)	Samples 1	2	3	Average
0.3	0.0013	0.0009	0.0004	0.0009
0.5	0.0013	0.0009	0.0004	0.0009
0.7	0.0023	0.0015	0.0011	0.0016
0.9	0.0031	0.0021	0.0021	0.0024
1.1	0.0040	0.0031	0.0028	0.0033
1.3	0.0051	0.0040	0.0037	0.0043
1.5	0.0052	0.0053	0.0055	0.0053
1.7	0.0063	0.0041	0.0030	0.0045

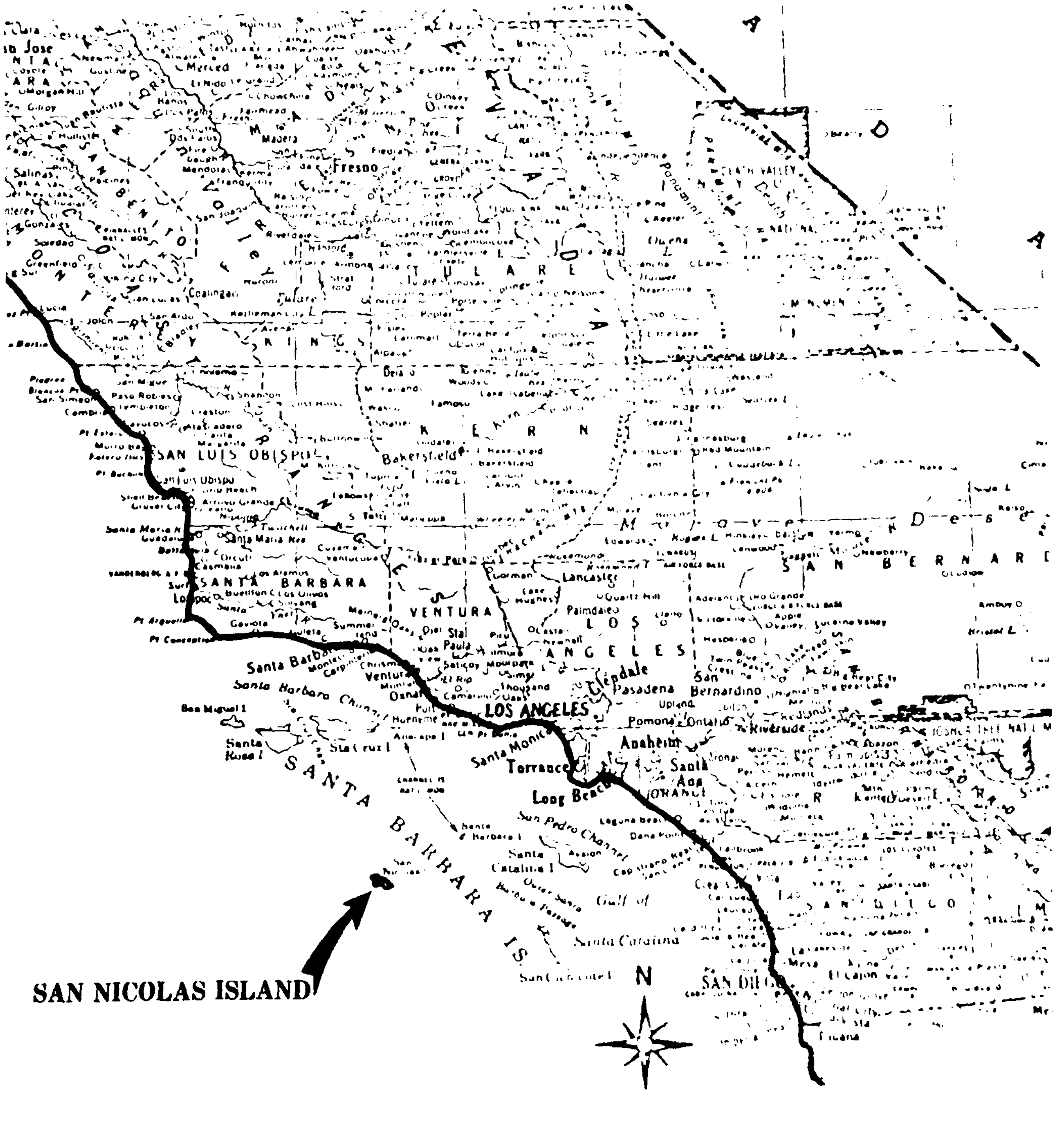
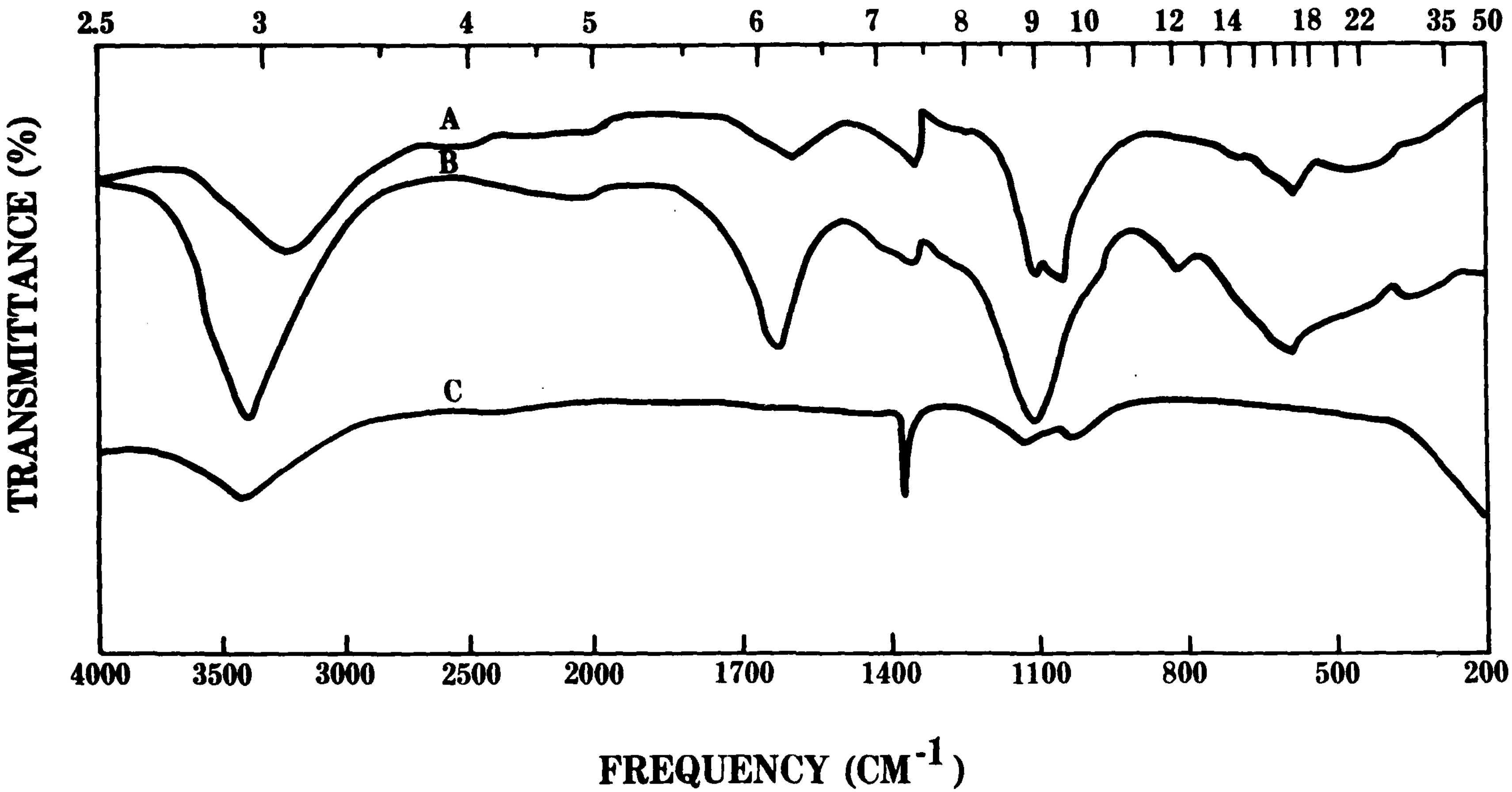


Figure 1. San Nicolas Island and California coastline.

Figure 2. San Nicolas Island, California.



A = SAMPLES 1 and 2

B = SAMPLE 3

C = SAMPLES 6 THROUGH 10

Figure 3. San Nicolas Island Spectrophotometric "fingerprints" wavelength microns.

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1. Petracca, C., and J. Lindberg, 1975, Installation and Operation of an Atmospheric Particulate Collector, ECOM 5575, Atmospheric Sciences Laboratory, White Sands Missile Range, New Mexico.

2. Lindberg, J. D., and L. S. Laude, 1974, Measurement of the Absorption Coefficient of Atmospheric Dust, Applied Optics, 13:1923-1927.

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7. Matthews, G. B., and B. E. Williams, compilers, 1978, Atmospheric Transmission and supporting Meteorology in the Marine Environment at San Nicolas Island, Semiannual Report TP-79-19, Pacific Missile Test Range, Point Mugu, California.

8. Kraus, E. H., W. F. Hunt, and L. S. Ramsdell, 1959, Mineralogy, McGraw-Hill Book Company, Inc., New York.

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APPENDIX[1]

SAN NICOLAS ISLAND PREVAILING METEOROLOGICAL CONDITIONS

During much of 1969, the North Pacific subtropical anticyclone and the Aleutian Low have been dominant factors in the weather at SNI, providing a nearly constant flow of air from the northwest. Based on a comprehensive airflow study conducted by the US Weather Bureau,[2] average streamlines constructed for the midseason months for both morning and afternoon periods reveal a persistent northwest flow at SNI which is nearly perpendicular to the overwater transmission paths. Offshore land breezes typical in morning hours along the mainland coast are replaced by afternoon onshore seabreezes, but winds at SNI are, on the average, identical for both time periods, indicating minimal diurnal influence of the continent on the surface wind patterns at SNI.

During the milder months, the marine layer is sharply defined with a strong inversion layer separating the cool, moist air below from warmer, subsidence-dried air above. This condition is quite typical of Mediterranean and subtropical climates. It is within the moist marine stratum that strati of stratocumulus clouds, fog, and haze are observed. A wide range of marine and coastal aerosols and droplets are also observed, with a consequent wide range in visibility from near zero in fog to 30 mi (48.3 km) or better under drier, unsaturated conditions.

During the cooler months, the stable inversion layer is frequently destroyed as the polar front and associated storm tracks shift southward, weakening and displacing the subtropical high. Storms moving from the west bring periodic rains to SNI under well-defined frontal bands of low, middle, and high clouds. Strong, gusty, shifting winds frequently occur near frontal passage, providing a wide range of tubulence conditions on both a small and large scale. Occasionally, high pressure builds over the continental land mass to the east, resulting in a Santa Ana wind regime in which continental air masses flow offshore and reach SNI, sometimes extending their effects over 1800 km (1,100 mi) to sea. In these respects, these offshore winds approximate outbreaks of dry air from the east coast of the US, as well as conditions observed over the Mediterranean, the Persian Gulf, and from the African continent. Some modified continental effects are observed at times when air masses move offshore from northern or central California and then traverse an overwater path of a few hundred miles before reaching SNI.

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[1]Robert deViolini, 1975, Climatic Summary for the Pacific Missile Test Center, TP-75-25, Pacific Missile Test Center, Point Mugu, California

[2]DeMarrais, Holzworth, and Hosler, 1965, Meteorological Summaries Pertinent to Atmospheric Transport and Diffusion over Southern California, US Weather Bureau Technical Paper No. 54, Department of Commerce

The predominance of the marine influence at SNI is well reflected in long-term climatologies derived from the official airfield weather station observations on the island. These climatologies are based on 25 years of records.[3] As shown in table 1, relative humidities average from a low of about 60 percent to a high of nearly 90 percent for all months, with minor month-to-month variation. The relative humidity has reached 100 percent in all months. On the northern end of the island, at the meteorological and transmission sites of the METR, relative humidity averages higher than at the higher airfield station, which is 502 ft (153 m) msl.

The persistence of the northwesterly overocean flow is also reflected in table 1, which shows that the prevailing wind direction is from the northwest in all months, and that the peak windspeeds in each month are from a northwest, west-northwest, or north direction, over the water. Mean sky cover averages near 5/10 throughout the year (slightly higher during the summer stratus season).

In the morning hours, the maritime winds are mixed with continental winds off the western coast of California (figure A-1). This mixing is a rouce of continental aerosol contamination into the near coastal regions; however, during the afternoon hours, the atmospheric condition causing the morning wind circulation is dissipated. This dissipation allows the coastal region to be swept by the northwesterly winds to purge the coastal region atmosphere of continental aerosol contaminations (figure A-2).

[3]G. B. Matthews and B. E. Williams, 1978, Atmospheric Transmission and Supporting Meteorology in the Marine Environment at San Nicolas Island, Semiannual Report TP-79-19, Pacific Missile Test Range, Point Mugu, California

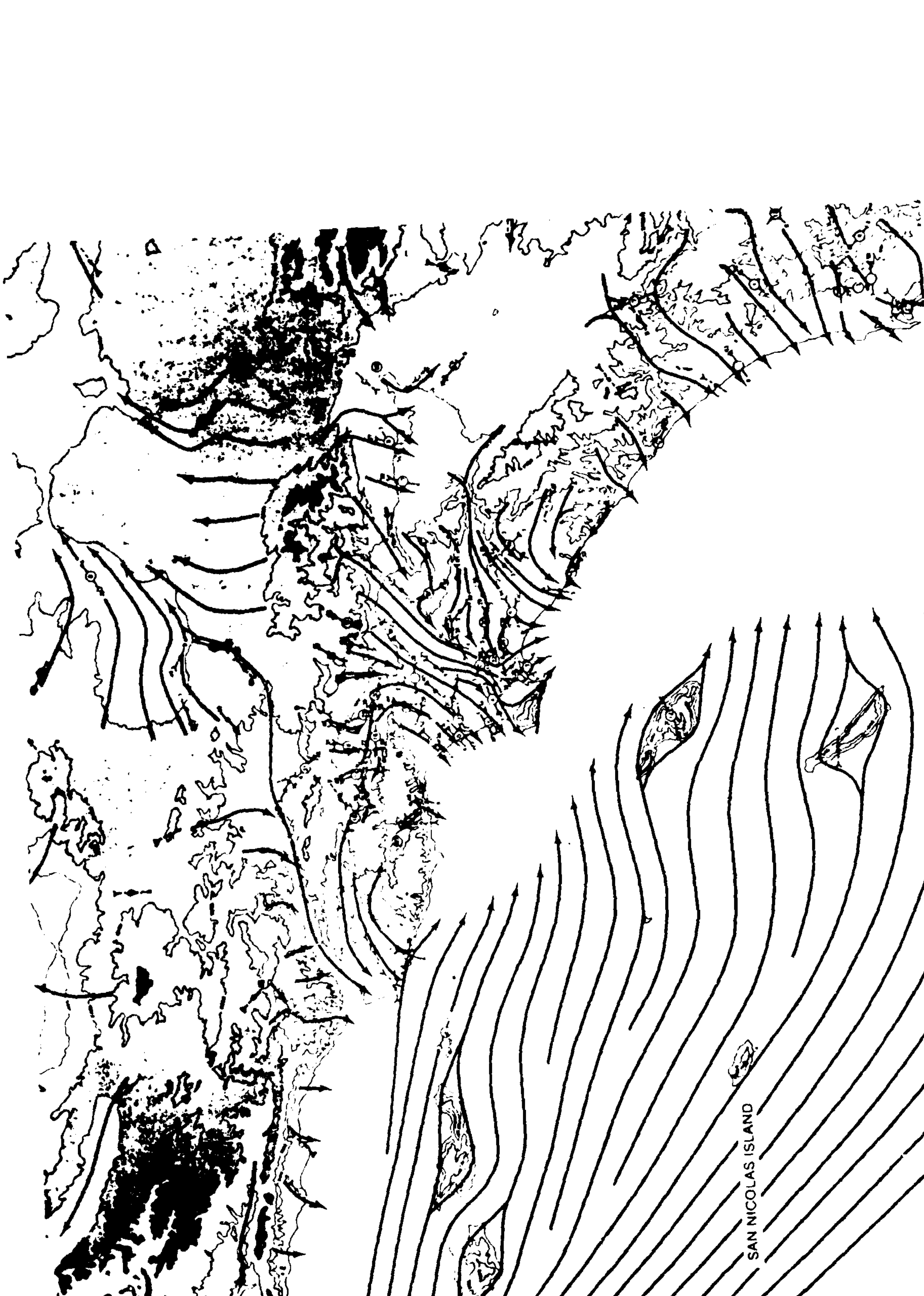

Figure A-1. Typical morning wind streamline pattern off the southern California coastline.

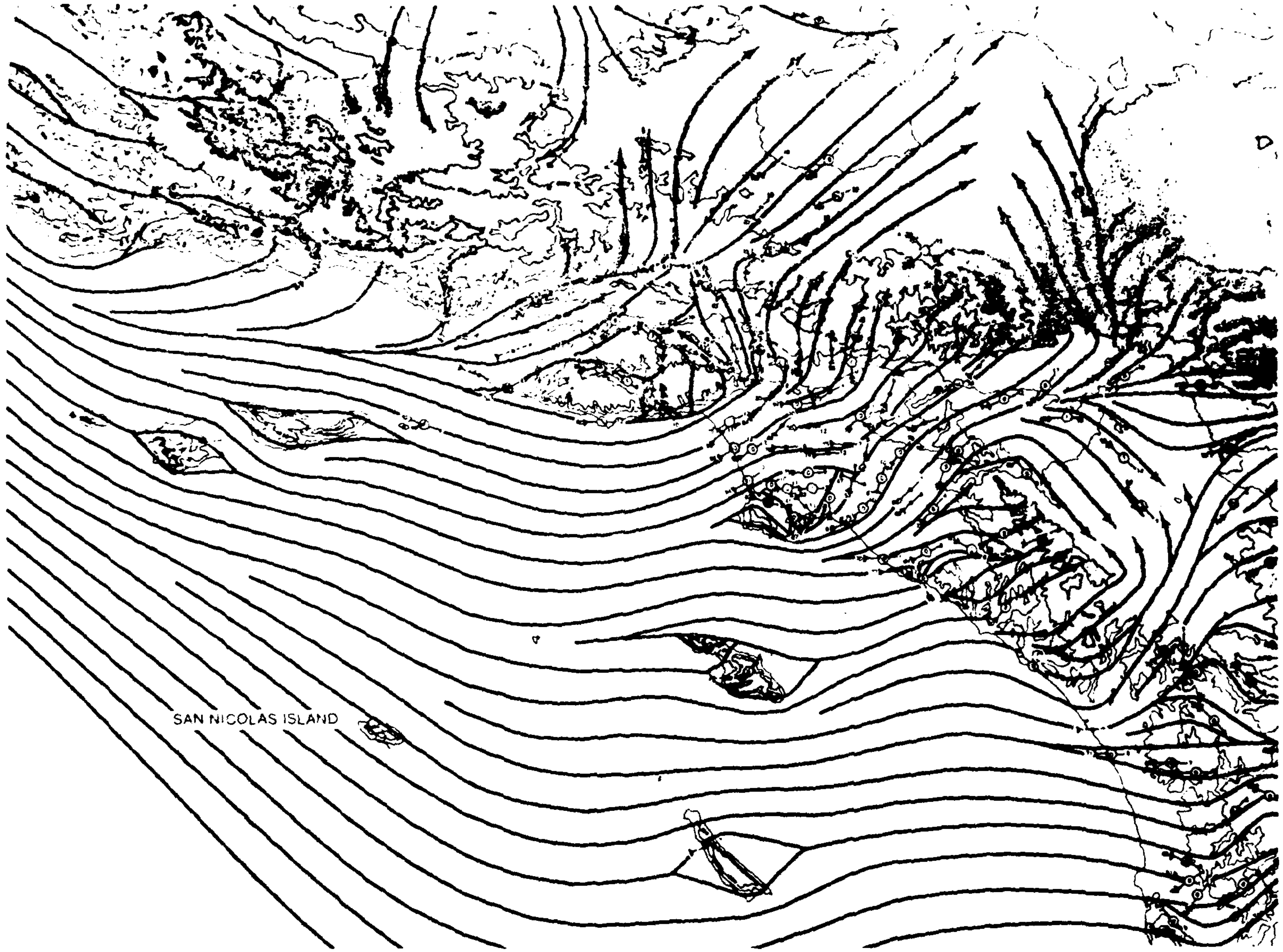

Figure A-2. Typical afternoon wind streamline pattern off the southern California coastline.

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2. DeMarrais, Holzworth, and Hosler, 1965, Meteorological Summaries Pertinent to Atmospheric Transport and Diffusion over Southern California, US Weather Bureau Technical Paper No. 54, Department of Commerce.

3. Matthews, G. B., and B. E. Williams, 1978, Atmospheric Transmission and Supporting Meteorology in the Marine Environment at San Nicolas Island, Semiannual Report TP-79-19, Pacific Missile Test Range, Point Mugu, California.

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Dr. Frank D. Eaton
Geophysical Institute
University of Alaska
Fairbanks, AK 99701

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